

(21) Application No 8107358
(22) Date of filing 9 Mar 1981
(30) Priority data
(31) 80/07972
(32) 10 Mar 1980
(33) United Kingdom (GB)
(43) Application published
16 Sep 1981
(51) INT CL³
C01F 11/00
(52) Domestic classification
C1A 32B 329 331 529 D37
G47 G47D34 G47D37 PB5
VG4
C1B 3C3 3CX 3F1 4
(56) Documents cited
GB 1138318
GB 980770
(58) Field of search
C1A
C1B
C7U
(71) Applicants
Harmerhill International
Limited,
Colenso House,
Deans Lane,
Pocklington,
York,
YO4 2PX.
(72) Inventors
Geoffrey Philip Adams,
Kevin Moran,
Keith William Morris,
Vivian Beverley Warne,
Pauline Ruth Wood.
(74) Agents
Pollak Mercer & Tench,
High Holborn House,
52/54 High Holborn,
London, WC1V 6RY.

(54) Chemical compositions, their manufacture and use in improving the storage characteristics of apples and pears

(57) Stable concentrated acidic formulations containing calcium ions and phosphate ions, in the weight/volume ranges of 1.9% to 5.0% and 7% to 40% respectively, are made by dissolving a source or sources of those ions in an aqueous acidic medium, for instance, in the presence of orthophosphoric acid, and then effecting controlled reduction of the acidity, e.g. to pH 1.6 to 2.0, by adding alkali. A surfactant is preferably included. On dilution with water, the formulations remain stable and can be converted into equally stable formulations which can be applied to fruit trees, the reduced acidity avoiding damage to the tree leaves. Take-up of the formulations by the trees results in fruit which is less prone to defects and is more storage-stable.

SPECIFICATION

Chemical compositions, their manufacture and use in improving the storage characteristics of apples and pears

5 This invention relates to chemical compositions in the form of stable phosphate formulations and is particularly concerned with phosphate formulations for agricultural purposes.

Although low temperatures are commonly used for the preservation of vegetable products, it is known that many products cannot be stored satisfactorily. For instance, fruit such as apples and pears undergoes breakdown in cold storage. Several varieties of apples and pears are so susceptible that as much as 45% of a stored crop can be lost for this reason. It is also known that resistance to low-temperature break-down can be imparted by the use of phosphate formulations, typically used as dilute water-based foliar spray compositions which are applied to the trees from which the fruit is later picked. The application of a phosphate formulation by this technique is efficient, as the phosphates are taken up by absorption through the leaves and fruit, and is much more effective than, say, the application of liquid or powder formulations to the ground.

10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000

The use of foliar spray compositions is effective in reducing losses due to breakdown of the fruit under cold storage conditions, but is not wholly successful and also has attendant disadvantages. For example, the defect known as bitter pit often increases. It is thought that this is due to the affinity of phosphate ions, applied as potassium, ammonium or other water-soluble phosphates, for calcium ions, because bitter pit is associated with low calcium contents adjacent the skin of apples and pears. Although the use of a water-based sprayable phosphate formulation, containing e.g. potassium hydrogen phosphate, leads to fruit which is more resistant to breakdown at low temperatures, the increased incidence of bitter pit militates against the use of such formulations. It is expected that these storage disorders can be prevented by incorporating both calcium ions and phosphate ions in the water-based formulation sprayed on to the trees, but calcium phosphates have no or only low water solubilities and phosphate ion concentrations of acceptably high levels can only be achieved with aqueous acid formulations of such low pH values that scorch damage to the trees occurs. There is thus a distinct need for formulations having high calcium and phosphate ion concentrations, together with reduced acidity levels and satisfactory stability in storage, which formulations, moreover, are capable of being readily diluted to give satisfactory sprayable compositions, for direct application to tree foliage.

It has now been discovered that effective phosphate compositions having this advantageous range of properties can be achieved by adopting a particular technique when making the composition.

According to one aspect of this invention, a method is provided of making a stable composition containing 35 in solution from 7% to 40% weight/volume of phosphate ions and from 1.9% to 5.0% weight/volume of calcium, which comprises forming an aqueous acidic solution containing phosphate ions and a source of calcium ions and adding an aqueous alkali solution to the aqueous acidic solution under such conditions than its acidity is reduced while complete dissolution is maintained. Preferably, a surfactant, for instance an alkyl imidazoline, is then included in the resultant composition. The surfactant has the advantage that the 40 resultant concentrated formulation is complete and can also be easily converted into a stable sprayable formulation by simple dilution with water. Moreover, the sprayable formulation obtained by diluting the concentrate has the ability to wet the leaf and fruit surfaces of trees to which it is applied and the surfactant also ensures that the solution spreads over the leaves and fruit.

According to a preferred feature of the invention, the source of calcium ions is a calcium compound, for 45 instance calcium hydroxide, which is dissolved in an aqueous acidic medium and undergoes a chemical reaction as it dissolves. Preferably, the source of calcium ions is dissolved in an aqueous orthophosphoric acid solution and the latter provides at least part of the phosphate content of the stable composition. A solution which contains 7% to 40%, most preferably 31.5%, by volume of orthophosphoric acid is desirably used. Preferably the calcium compound is added, with rapid stirring, so as to give a final concentration 50 within the range from 3.6% to 9.5%, preferably 6% to 9% and most preferably 7.3% weight/volume, calculated as $\text{Ca}(\text{OH})_2$. The acidity of such a composition is indicated by its very low pH, a typical pH range being 0.8 to 1.5. This high acidity makes the composition too acid to apply to the leaves and other parts of trees, even after dilution to the required concentration for application, because of the scorch damage which such an acidic formulation would cause. The pH of the composition is accordingly adjusted by the addition of 55 the aqueous alkali solution. It is essential to make this addition so that the composition remains in a state of complete dissolution. Typically, the alkali solution is a 40% weight/volume solution of caustic soda. In general the amount of concentration of the alkali solution used is controlled so that the very low pH of the concentrate, usually 0.8 to 1.5 as noted above, is raised and the resultant stable composition, containing the high pH phosphate and calcium contents indicated, has a pH of, typically, 1.6 to 2.0 and, preferably, a pH at or slightly above 1.7, i.e. a pH of 1.7 to 1.8.

According to a further preferred feature of the invention, one or more compounds comprising the source of calcium ions and also a source of phosphate ions is/are dissolved in an aqueous acidic medium and the one or more compounds provide at least part of the phosphate content of the stable composition. In one form of this feature of the method, the source of calcium ions and the source of phosphate ions comprise a calcium phosphate component which is dissolved in the aqueous acidic medium. The aqueous acidic

medium may comprise either or both of orthophosphoric acid and hydrochloric acid. For instance, in a preferred form of the method, the aqueous acidic medium comprises a solution containing 4% to 5% by volume of 85.5% orthophosphoric acid, and 10% to 15% by volume of 28% hydrochloric acid. The acidity lies in the range indicated above if the stable solution is formed in the manner just described.

5 The invention is based upon the unexpected discovery that the high levels of acidity believed necessary to obtain concentrated solutions of phosphate ions and calcium ions can surprisingly be reduced, by the careful addition of alkali in solution, without causing precipitation or otherwise producing instability of the composition. Calcium salts of the various phosphoric acids are only slightly soluble in water. It has now been found that the use of normal techniques, including continuous stirring and the slow and careful addition of 10 one component to another, allows solutions containing both calcium ions and phosphate ions, whether provided by orthophosphoric acid alone or in conjunction with other sources of phosphate ions, or by such other sources of phosphate ions alone, such solutions thus constituting stable aqueous acid solutions of calcium phosphate, to be reduced in acidity without losing stability and, in particular, while complete dissolution of the calcium phosphate component is maintained.

15 It is highly desirable for the surfactant to be included when the concentrated composition is manufactured. The surfactant, which acts as a wetting and spreading agent, could also be added after dilution of the concentrate with water to prepare it for use as a foliar spray. However it is very much preferred for the dilution step to be made as simple as possible, so that the spray formulation ready for use is produced in one simple step by combining a given quantity of the concentrate with a given quantity of water. This is

20 especially important when consideration is given to the circumstances likely to apply when the dilution step is being carried out, whereby drums or other containers of the concentrate have their contents emptied into a mixing tank, together with water, adjacent the orchard where the trees are to be treated. It is thus preferable to incorporate the wetting agent or surfactant in the concentrate, so that the product delivered to the user is a stable clear concentrated solution containing calcium ions, phosphate ions and a surfactant,

25 which only requires mixing in the appropriate proportion with clean water to become a clear stable sprayable formulation. The wetting agent should have the following properties. It must not be phyto-toxic. It must be stable and remain stable in the solution. It must not affect the pH of the solution to any great extent. It must not have a detrimental effect on the stability, appearance or storage characteristics of the solution. It must improve the ability of the solution to 'wet' surfaces usually by lowering the surface tension of the

30 solution. It should not have excessive foaming characteristics. Preferred surfactants include organo-sulphonate detergents, particularly the various sodium alkyl-benzene sulphonates marketed under the Regd. Trademark "NANSA", and the various alkyl-imidazoline compounds. An especially preferred surfactant is 2-caprylyl-1-(ethyl-betaoxypropanoic acid)-imidazoline. The selected surfactant is preferably dissolved in the concentrated solution to give a concentration within the range 0.05%-5.00% w/v. Particularly suitable

35 products are those marketed under the Regd. Trademark "CRODATERIC". According to another preferred feature of the invention, the phosphate concentration of the stable composition is in the range from 28% to 35% weight/volume calculated as P_2O_5 , while the calcium content is in the range from 3.7% to 4.2% weight/volume.

The stable concentrated solution of the invention is capable of dilution to produce a stable foliar spray 40 composition, having a pH suitable for safe application to fruit trees, the phosphate concentration of the sprayable formulation preferably being in the range from 0.07% to 1.25% weight/volume and, most preferably, 0.28% to 0.65% weight/volume, calculated as P_2O_5 . The calcium concentration in the sprayable formulation preferably is in the range from 0.03% to 0.34% weight/volume and, most preferably, 0.037% to 0.16% weight/volume.

45 In order to illustrate the invention, examples are given below of the manufacture of preferred forms of phosphate composition and of the improved results obtained after use; Example 1 relates to a composition in which the acid provides all the phosphate ion and Example 2 relates to a composition in which the phosphate ion is provided partly by the acid and partly as calcium phosphate.

50 EXAMPLE 1

Preparation of high-phosphate composition

An acid phosphate component was made by slowly stirring 625 l water in a mixing vessel having a capacity of at least 1,000 l and then carefully adding 505 kg of 85.5% w/v orthophosphoric acid. The rate of stirring was then increased and 73 kg calcium hydroxide were added. The mixture was stirred vigorously 55 until all the calcium hydroxide had undergone reaction and thus had dissolved and the mixture was clear. The solution has a volume of approximately 920 l and a pH of 1.2.

The 40% w/v caustic soda solution was then added slowly, while continuing to stir the mixture, until the pH reached 1.7, giving a final volume of approximately 960 l.

0.5 kg of surfactant (e.g. the 2-caprylyl-1-(ethyl-betaoxypropanoic acid)-imidazoline product marketed by 60 Croda under the Regd. Trademark "CRODATERIC CY Na 50") was added while stirring was continued. Water was then added to adjust the volume to 1000 litres. This solution contained 3.85% w/v calcium and 31.3% w/v phosphate.

The resulting formulation is stable under storage at ambient temperature over extended periods and can be readily diluted with water to give sprayable compositions of adequate phosphate concentration which are 65 themselves stable and also safe to use.

EXAMPLE 2*Preparation of high-phosphate composition*

An acid phosphate component was made by slowly stirring 585 l water in a mixing vessel having a capacity of at least 1,000 l and then carefully adding 79 l of 28% hydrochloric acid, followed by 31 l (52 kg) of

5 orthophosphoric acid. The rate of stirring was then increased and portions of acid calcium phosphate were slowly added, ensuring that each portion was fully dissolved before adding the next, until a total of 218 kg had been added. The resultant acid phosphate component had a volume of 770 l, a phosphate ion concentration of 20.2% w/v (calculated as P_2O_5) and a pH of 1.0. (The acid calcium phosphate used was one which assays not less than 80% Ca (H_2PO_4)₂ and also contains dicalcium phosphate; the latter becomes

10 converted by phosphoric acid to the more soluble monocalcium phosphate. A suitable form of this calcium phosphate is that marketed by Albright & Wilson Limited, under the Regd. Trademark "IBEX".)

An alkali component was made by slowly stirring approximately 170 l of water in a mixing vessel having a capacity of at least 200 l and adding 22.8 kg of caustic soda in portions; when all the caustic soda had dissolved, further water was added to bring the final volume of the alkali component of 190 l; the alkali

15 component formulated in this way had a concentration of approximately 12% w/v. This solution was then slowly added to the phosphate component, while continuing to stir the latter, until the pH reached 2.0, giving a final volume of approximately 960 l.

20 A surfactant component was made up by dissolving 210 g of 80% active sodium dodecyl benzene sulphonate powder (e.g. the product marketed by Marchon under the Regd. Trademark "NANSA HS80/S") in 20 l of water and this was then added to the pH-adjusted phosphate formulation. Water was then added to adjust the volume to 1,000 litres. This solution contained 3.9% w/v calcium and 15.5% w/v phosphate.

The resulting formulation is stable under storage at ambient temperature over extended periods and can be readily diluted with water to give sprayable compositions of adequate phosphate concentration which are themselves stable and also safe to use.

25 *Effect of diluted high-phosphate sprays on fruit and its storage*

In order to evaluate the effect of compositions according to the invention, when diluted for use as foliar sprays, field trials have been carried out in recent years. Three examples are given below.

30 EXAMPLE 3

On apple trees of the variety Cox's Orange Pippin in a large replicated experiment, the following treatments were included.

- (i) Diluted formulation containing 0.17% w/v Ca, 0.61% w/v P_2O_5 .
- (ii) Diluted formulation containing 0.34% w/v Ca, 1.22% w/v P_2O_5 .
- 35 (iii) (i) Included in a calcium chloride (0.6% w/v) spray programme.
- (iv) Untreated control

The diluted formulation was obtained by appropriately mixing water with the concentrated formulation made as described in Example 2. In the case of all the treatments the trees were subjected to six sprays, commencing shortly after petal fall, and applied at intervals of 10 – 15 days.

40 Fruit analysis at harvest gave the following data:

		Fruit Ca	Fruit P (mg/100g Fresh Fruit)	
45	(i)	5.50	12.67	45
	(ii)	5.73	12.88	
	(iii)	6.83	13.96	
50	(iv)	5.87	11.95	50

In addition there were indications that yields may have been improved in treatments (i) and (ii). Essentially similar favourable results were obtained by the use of a spray formulation made from the concentrate of Example 1.

EXAMPLE 4

On apple trees of the variety Bramley's Seedling in a large replicated experiment, the following treatments 60 were included:

(i) 4 early sprays of diluted formulation containing 0.17% w/v Ca, 0.61% w/v P_2O_5 ; treatment times as in

Example 3;

(ii) 4 late sprays of diluted formulation containing 0.17% w/v Ca, 0.61% w/v P_2O_5 (as in Example 3) commencing mid-July;

65 (iii) 4 early sprays of diluted formulation containing 0.17% w/v Ca, 0.61% w/v P_2O_5 (as in Example 3)

followed by 2 sprays with 0.6% w/v calcium chloride;
 (iv) 4 early sprays of diluted formulation containing 0.34% w/v Ca, 1.22% w/v P₂O₅ (as in Example 3)

followed by 2 sprays with 0.6% w/v calcium chloride;

(v) untreated control.

5 The concentrate used to make the diluted formulation was that of Example 2.

Fruit analyses at harvest gave the following data:

	Fruit Ca	Fruit P (mg/100g Fresh Fruit)
10 (i)	5.35	19.7
15 (ii)	4.30	19.9
15 (iii)	5.70	10.0
20 (iv)	4.90	11.6
	(v)	4.10
		18.9

In all of the experiments summarised in Examples 3 and 4, increases in fruit P are consistently shown, whilst fruit Ca remains at the same level or increases.

Storage data from a third trial gave indications of the reduction of nutritionally-related storage disorders.

25 EXAMPLE 5

In a very large replicated experiment on Bramley's Seedling apples the following treatments, again based upon the use of the concentrate of Example 2, were included:

(i) 4 early sprays diluted formulation containing 0.17% w/v Ca, 0.61% w/v P₂O₅ (as in Example 3);

30 (ii) 4 late sprays diluted formulation containing 0.17% w/v Ca, 0.61% w/v P₂O₅ (as in Example 3);
 (iii) untreated control.

Fruit were stored in 8-10% CO₂ at 1.5°C for several months and in May examinations gave the following results:

	Low Temperature Breakdown	Bitter Pit
	%	%
35 (i)	33.8	0.5
40 (ii)	34.3	2.0
	(iii)	43.0
		2.5

45 Improvements in fruit storage have thus been demonstrated. The data in the above Examples also show that the concentrated compositions of the invention, having high phosphate levels, are capable of conversion by simple dilution to sprayable formulations which are themselves stable, like the concentrates, and also are very effective in giving improved storability to fruit, e.g. apples and pears, grown on trees treated with the formulations. The high concentration and the stability of the concentrated compositions

50 avoids the need for transport of large volumes of dilute compositions.

CLAIMS

1. A method of making a stable composition containing in solution from 7% to 40% weight/volume of phosphate ions and from 1.9% to 5.0% weight/volume of calcium, which comprises forming an aqueous acidic solution containing phosphate ions and a source of calcium ions and adding an aqueous alkali solution to the aqueous acidic solution under such conditions that its acidity is reduced while complete dissolution is maintained.

55 2. A method according to claim 1, wherein the source of calcium ions is a calcium compound which is dissolved in an aqueous acidic medium and undergoes a chemical reaction as it dissolves.

60 3. A method according to claim 2, wherein the source of calcium ions is dissolved in an aqueous orthophosphoric acid solution and the latter provides at least part of the phosphate content of the stable composition.

65 4. A method according to claim 3, wherein the orthophosphoric acid solution contains 7% to 40% by volume of 85.5% orthophosphoric acid.

5. A method according to claim 2, 3 or 4, wherein the source of calcium ions is calcium hydroxide.
6. A method according to claim 1, wherein one or more compounds comprising the source of calcium ions and also a source of phosphate ions is/are dissolved in an aqueous acidic medium and the one or more compounds provide at least part of the phosphate content of the stable composition.
- 5 7. A method according to claim 6, wherein the source of calcium ions and source of phosphate ions comprise a calcium phosphate component which is dissolved in the aqueous acidic medium.
8. A method according to claim 6 or 7, wherein the aqueous acidic medium comprises orthophosphoric acid.
9. A method according to claim 6, 7 or 8, wherein the aqueous acidic medium comprises hydrochloric acid.
- 10 10. A method according to claim 9, wherein the aqueous acidic medium comprises a solution containing 4% to 5% by volume of 85.5% orthophosphoric acid and 10% to 15% by volume of 28% hydrochloric acid.
11. A method according to any preceding claim, wherein a surfactant is included in the resultant composition.
- 15 12. A method according to claim 11, wherein the surfactant is selected from organo-sulphonate and alkylimidazoline compounds.
13. A method according to claim 11 or 12, wherein the surfactant comprises 0.05% to 5.00% weight/volume of the stable composition.
14. A method according to any preceding claim, wherein the composition is made so as to have a pH of 20 1.6 to 2.0.
15. A method according to claim 14, wherein the composition has a pH of 1.7 to 1.8.
16. A method according to any preceding claim, substantially as described with reference to the foregoing Examples.
- 25 17. A stable composition capable of dilution with water to give a stable sprayable formulation, which comprises 7% to 40% weight/volume of phosphate and 1.9% to 5.0% weight/volume of calcium and, optionally, 0.05% to 5.00% weight/volume of a surfactant, the composition having a pH of 1.6 to 2.0.
18. A composition according to claim 17, when made by a method according to any of claims 1 to 16.
19. A method of treating fruit trees, which comprises forming a sprayable stable formulation by diluting with water a composition according to claim 17 or 18 and applying the diluted formulation to the leaves and 30 fruit of the trees after petal fall.
20. A method according to claim 19, wherein the composition is diluted so that the sprayable formulation has a phosphate concentration in the range from 0.07% to 1.25% weight/volume and a calcium concentration in the range from 0.03% to 0.34% weight/volume.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.